

interpose between the helices. The effect of this is to impede the re-formation of the lamellar structure upon cooling. Thus the critical temperature is lower for maize than for waxy maize, for which the lack of amylose removes this specific problem.

Conclusions

Scattering techniques are proving very powerful in discovering how the internal order within starch granules is affected by external parameters. Using a combination of SAXS and SANS, as well as WAXS data, it is becoming possible to understand the factors that determine how the granular structure breaks down during processing. With the advent of new starch cultivars and mutants it is increasingly important to rationalise the factors which are important in controlling structure, so that optimisation of the utilisation of starch can be achieved. Scattering techniques provide one approach to providing this information.

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Structure of Block Copolymer Solutions

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The addition of solvent to a diblock copolymer melt affects a variety of order-order transitions between different phases, as well as the order-to-disorder transition. The sequence of phases with dilution and/or heating may be anticipated qualitatively on the basis of diagonal trajectories across the melt phase map, but there are a variety of novel features as well. At sufficiently dilute concentrations, suspensions of micelles are observed, and the critical micelle temperature in dilute solution is similar to the order disorder temperature at intermediate concentrations.

Introduction

Block copolymers are a class of macromolecular surfactants that self-assemble into a variety of microstructures [1, 2]. In many applications, notably in adhesive formulations, block copolymers are diluted with low molecular weight additives to modify relevant mechanical properties such as tack. However, the ordered phase symmetry may also depend on diluent concentration and temperature. We are pursuing a systematic experimental assessment of the phase behavior of block copolymer solutions, utilizing a series of solvents of varying selectivity for the two blocks. The experimental results are also supported by self-consistent mean-field calculations of free energies. In this work we describe the effects of varying solvent selectivity on the phase behavior of a particular styrene-isoprene diblock copolymer.

Experimental

The styrene-isoprene (SI) diblock copolymer was synthesized by standard living anionic polymerization protocols, as previously described [3]. It has block molecular weights of 11,000 (S) and 21,000 (I), with an overall polydispersity of 1.04. The composition and molecular weight were established by NMR and size exclusion chromatography with light scattering detection, respectively. The solvents bis(2-ethylhexyl) phthalate (DOP), di-n-butyl phthalate (DBP), and di-

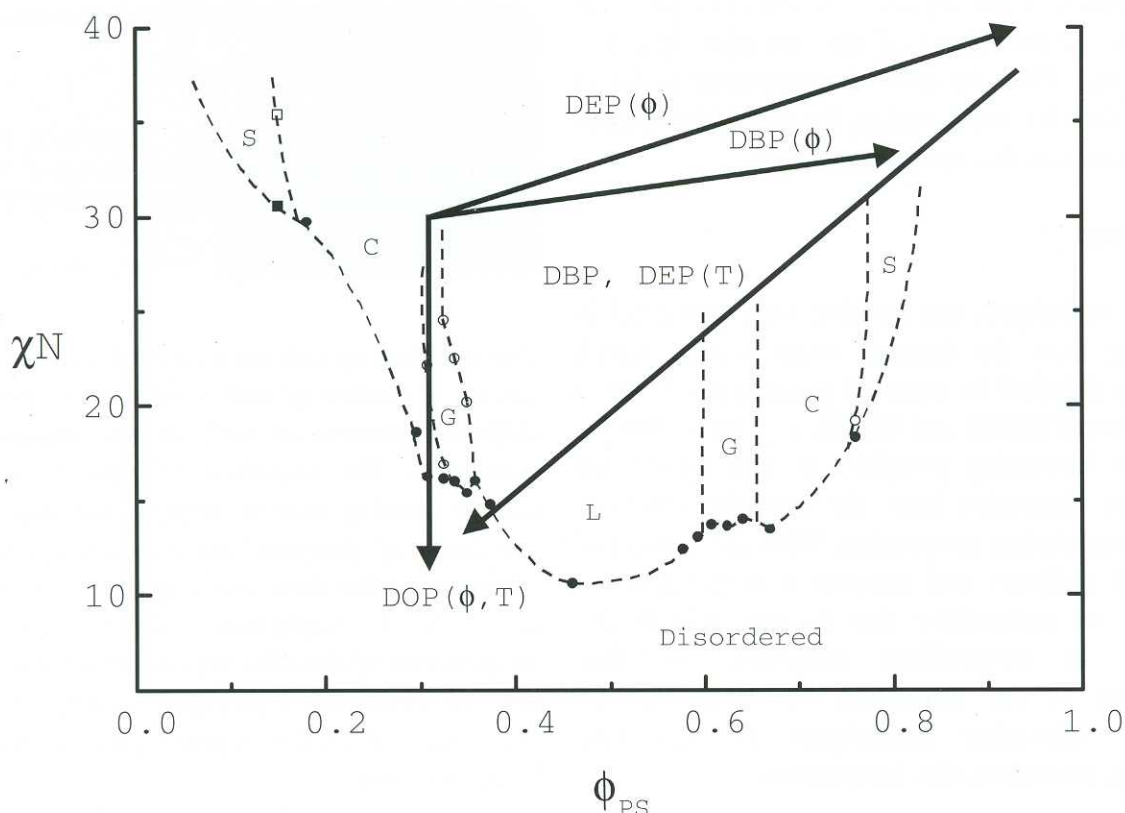


Figure 1: Phase map for styrene-isoprene diblock copolymers in the melt. The solid arrows indicate the qualitative effects of adding neutral (DOP) and slightly selective (DBP, DEP) solvents as a function of volume fraction (ϕ) and also of heating (T).

ethyl phthalate (DEP) were obtained from Aldrich and purified by neutralizing with 5% aqueous sodium bicarbonate, rinsing with distilled water, drying over calcium chloride, and vacuum distilling prior to use. Solutions were prepared gravimetrically, with methylene chloride as a co-solvent. The co-solvent was stripped off under vacuum, and polymer volume fractions, ϕ , calculated assuming additivity of volumes and densities of 0.981, 1.043, and 1.18 g/mL for DOP, DBP, and DEP, respectively.

The phase behavior was determined by a combination of small-angle X-ray scattering (SAXS), static birefringence, and rheology. SAXS measurements were taken on the University of Minnesota beamline, using Cu K_{α} radiation ($\lambda = 1.54$ Å) from a Rigaku RU-200BVH rotating anode and Franks mirror optics. Scattered X-rays were collected on an area detector (Siemens), corrected for detector response, and azimuthally averaged to give intensity I (arbitrary units) versus scattering wavevector q . Static birefringence measurements were made as previously described [3], utilizing a 5 mW HeNe laser, an initial polarizer, an orthogonal analyzer after the sample, and a photodiode detector.

For isotropic samples (either disordered or cubic phases) the transmitted depolarized intensity is essentially zero, but the lamellar and cylindrical phases depolarize the light to a finite extent. Thus SAXS is necessary to establish the symmetry of a given phase, but birefringence is a rapid way to locate thermotropic transitions. Rheology is also a standard means to locate transitions, as the low frequency shear elastic modulus is very sensitive to the state of order [4]. Measurements were taken on a Rheometric Scientific DSR in the parallel plate geometry. In all cases, transition temperatures located by two or more techniques were in quantitative agreement.

Results and Discussion

The phase behavior of diblock copolymer melts is reasonably well understood [1]. The experimental phase map for SI diblock copolymers is shown in Figure 1, and is largely consistent with other measurements on this system [5, 6]. Furthermore, the essential features (*i.e.*, identity and location of the particular ordered phases) is captured by self-consistent mean-field (SCMF) theory [7, 8]. The vertical axis is the product of the degree of

polymerization, N , and the styrene-isoprene interaction parameter, χ . The latter represents the heat of mixing per monomer unit, normalized by kT . The major morphologies are lamellae (L), cylinders of the minor component packed on a hexagonal lattice (C), and spherical micelles packed on a bcc lattice (S). The choice of structure is determined primarily by the volume fraction of one block, ϕ . A bicontinuous cubic phase, the gyroid (G, space group $Ia\bar{3}d$), is found for compositions between L and C, but only near the order-disorder transition (ODT) (A perforated layer (PL) or modulated layer (ML) phase is often seen near the G phase, but this is now understood as a metastable intermediate that will ultimately anneal into G [9]).

The qualitative effects of adding a solvent to a block copolymer melt are also illustrated by the arrows in Figure 1. If a solvent is neutral *i.e.* it is an equally good solvent for both blocks, the addition of solvent is analogous to increasing temperature. The dilution of contacts between monomers reduces the effective χ parameter. On the other hand, if a very selective solvent is employed, it will preferentially segregate into that microdomain. The resulting phases can be anticipated to some extent simply by computing a renormalized ϕ , assuming complete partitioning of the diluent. However, the χ parameter between the solvent and the unfavorable block often exceeds that between the two monomers, and thus the arrow indicates that the effective degree of segregation, χN , also increases with added solvent. Thus solvents with differing degrees of selectivity will move the system to lesser or greater degrees of segregation. Upon heating, another interesting situation develops. The solvent will generally become less selective, and therefore redistribute itself more uniformly between the microdomains, as T increases. Consequently, in contrast to the neutral solvent case, there will be a diagonal trajectory back across the phase map. A rich variety of lyotropic and thermotropic order-order transitions (OOT) should thus be accessible.

These qualitative features are all evident in measurements on SI(11-21) in DOP, DBP, and DEP, as shown in Figures 2(a), (b) and (c). In the melt, SI(11-21) exhibits an OOT from $G \rightarrow C$ upon heating, and the ODT at 238°C . At low T the PS glass transition intervenes and prevents further study of equilibrium phases. As DOP is a neutral solvent, both the ODT and OOT move to lower T as the solvent concentration increases, and no new structures are observed. However, one can see that the window of

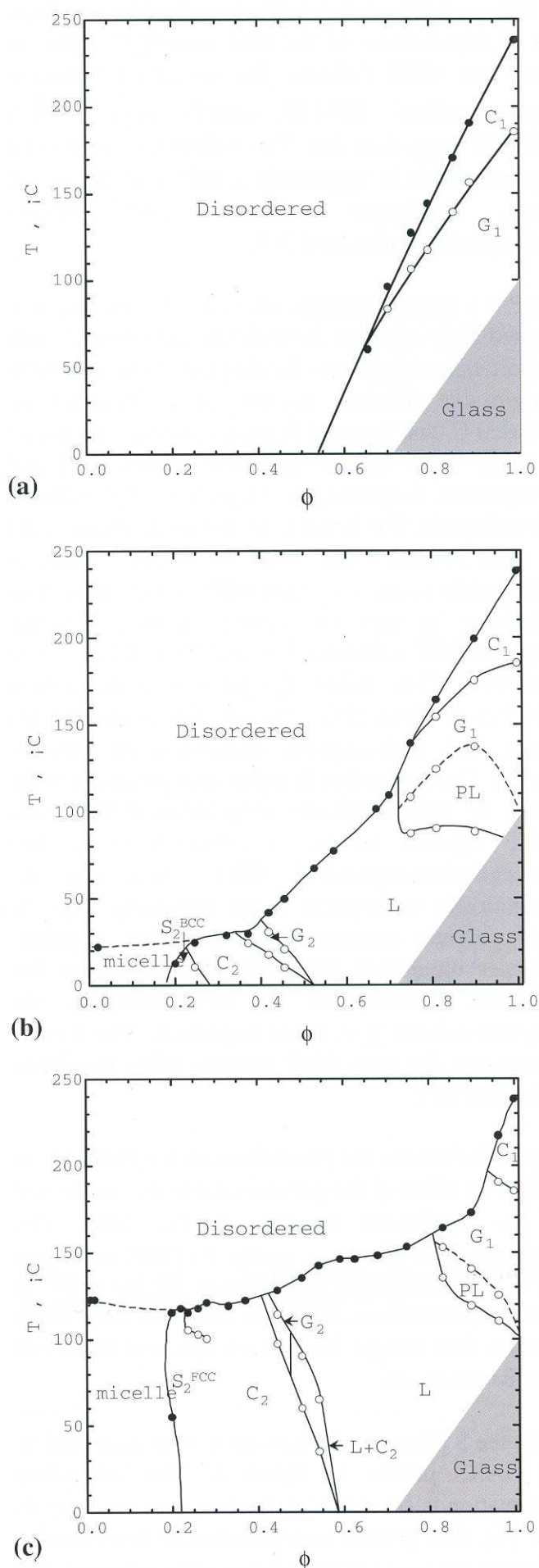


Figure 2: Phase diagrams for a styrene-isoprene diblock copolymer with block molecular weights of 11,000 and 21,000 dissolved in (a) DOP, (b) DBP, and (c) DEP.

C phase shrinks and disappears with dilution. Thus, the T dependences of the ODT and OOT differ. In fact, the OOT follows the so-called “dilution approximation” [10-12], namely $\chi_{OOT} \sim \phi^{-1}$, whereas χ_{ODT} does not. This failure of the dilution approximation is apparently a universal feature in block copolymer solutions, and remains incompletely understood [13].

DBP is a slightly styrene selective solvent, and it is immediately apparent from Figure 2(b) that this has important consequences for the phase behavior. With progressive dilution, regions of L, inverted G, inverted C, and inverted S phases appear. “Inverted” in this case means that the major polymer component, isoprene, is located in the smaller microdomain. The boundaries between phases tend to slant toward lower ϕ as T increases. This is attributable to the fact that DBP is becoming less selective; in fact the critical temperature for isoprene/DBP solutions has been estimated to be near 90°C [14]. When the polymer concentration falls below about 20%, the micelles no longer fill space, and a disordered suspension of micelles results. These micelles disperse into polymer chains above the critical micelle temperature (CMT). The CMT appears to be a continuation of the concentration-dependent ODT. This can be qualitatively understood in the following way. At high polymer concentrations, it is the polymer-polymer interaction parameter that dominates the behavior, whereas for low concentrations, the polymer-solvent χ is more important. The former determines the melt ODT and the latter the dilute solution CMT.

Figure 2(c) shows the phase diagram for SI(11-21) in DEP. The effect of the greater selectivity is reflected in the significant increase in the ODT. The progression of phases is similar to DBP, and again the CMT determines the location of the ODT at lower concentrations. However, there are some novel features that emerge for this solvent, and these will now be discussed.

First, the S phase is now fcc, not bcc, as indicated by the SAXS pattern in Figure 3. This interesting observation is consistent with some previous reports [15, 16]. One general interpretation of this behavior relies on the range of the intermicellar potential. For micelles with short corona blocks, the interaction is short-ranged, and just like hard spheres, the micelles select the close-packed fcc lattice. In the melt, it is

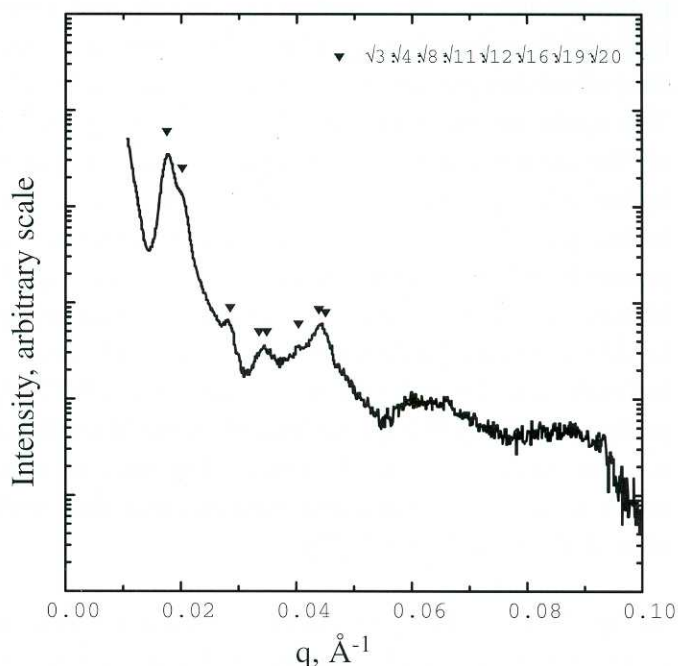


Figure 3: SAXS pattern for the $\phi = 0.26$ solution in DEP showing the allowed reflections for an fcc phase.

the major block that forms the corona, imparting a long-range interaction that favors the bcc arrangement. However, this argument is not sufficient to fully explain the results here, because in DBP at the same concentration, the spheres adopt the bcc lattice, whereas the coronal conformation should be the same.

Second, there is a re-entrant ordered phase for the solution with $\phi = 0.2$, namely below about 50°C the solution is a disordered suspension of micelles, but upon heating it transforms to an fcc lattice, before melting at the ODT near 120°C. This may be ascribed to swelling of the micelles. At low temperature the micelles are just on the brink of reaching the effective volume fraction necessary to order on a lattice. Upon heating, the solvent becomes less repelled by the isoprene cores, and the micelles swell. This is sufficient to induce the ordering transition, but as temperature increases the solvent dissolves the isoprene core and the solution melts.

Third, near $\phi = 0.55$, there is a wide region of coexisting L and C. The experimental signature of this is shown in Figure 4. The observation of a region of coexistence is not surprising in itself, given that it is a two-component system; in general one expects coexistence regions along each phase boundary. However, in all the other cases this region is

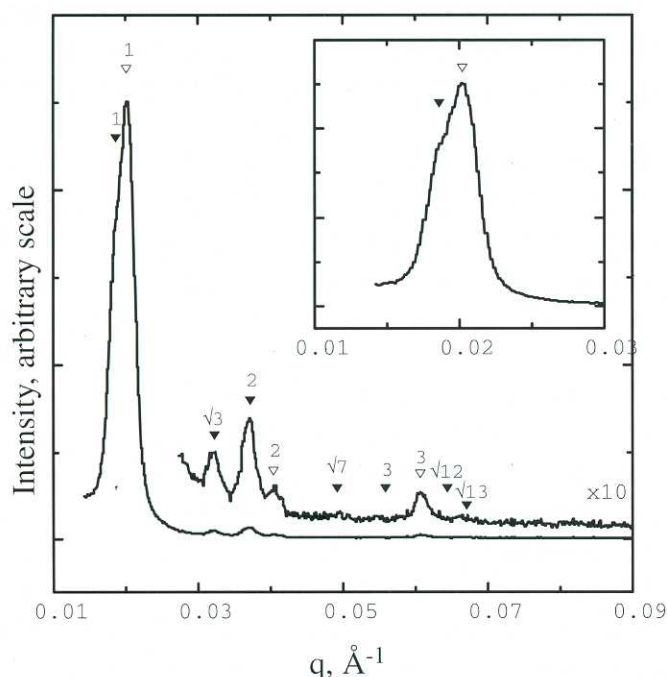


Figure 4: SAXS pattern for the $\phi = 0.54$ solution in DEP showing the coexisting lamellar and hexagonal phases.

extremely narrow, probably on the order of 1°C wide, whereas in this case the interval is as much as 40°C . This is presumably attributable to the subtle balance of chain stretching, packing frustration, and conformational asymmetry that ultimately determines the precise location of the phase boundary.

Summary

The addition of solvents of varying selectivity to a styrene-isoprene diblock copolymer reveals a rich array of lyotropic and thermotropic transitions. The sequence of ordered phases may be approximately anticipated by the concept of diagonal trajectories on the melt phase map, but important distinctions are also exposed.

Acknowledgements

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